



*Fluoride glass fiber sources:
Problems and prospects*

Marcel Poulain and Gwenael Mazé

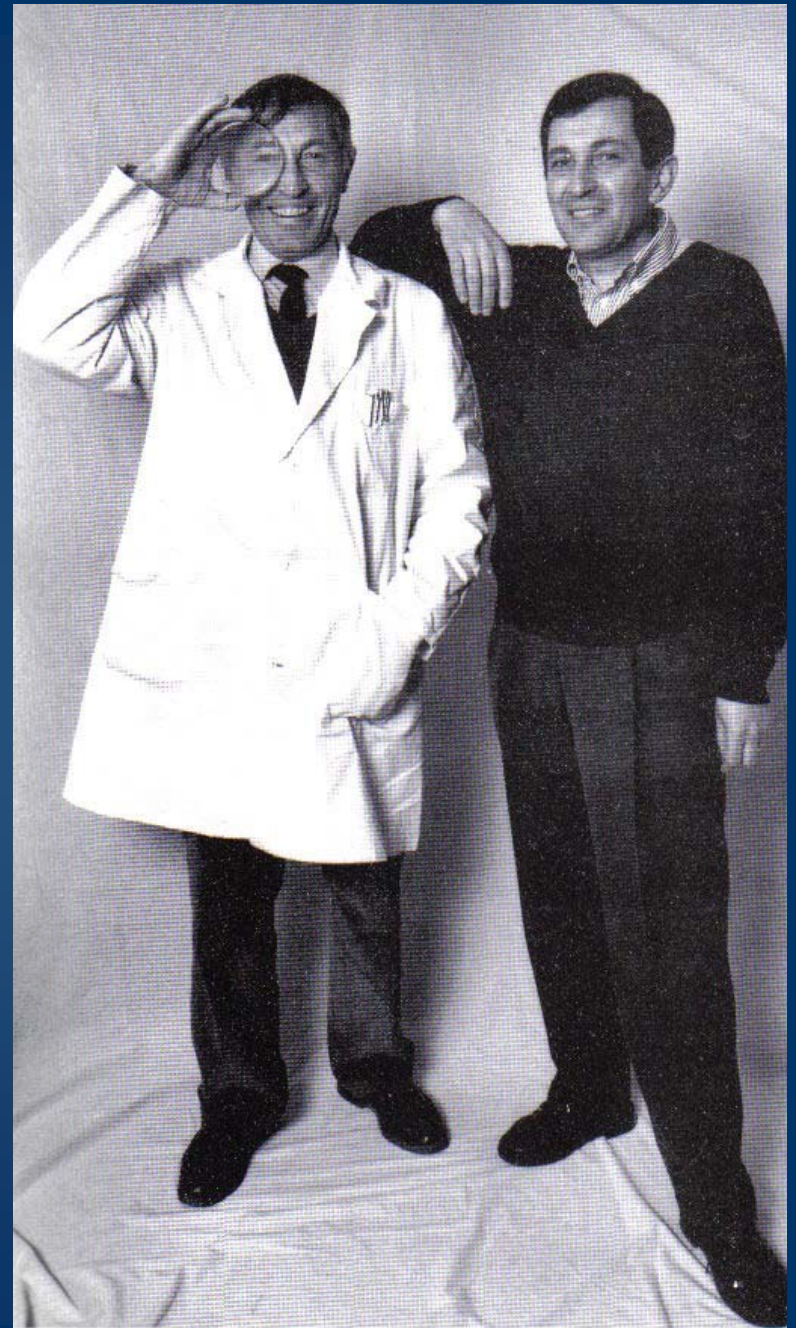
Rennes University and Le Verre Fluoré



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Outline :

- 1 Introduction**
- 2 Fluoride glass technology**
- 3 Specifications of active fibers**
- 4 Achievements**
- 5 Problems and prospects**
- 6 Conclusion**





INTRODUCTION

The privilege of experience...



36 years of continuous activity in fluoride glasses, from the discovery to the industrial development



Pioneering achievements



Interaction and collaborations with major actors of fiber lasers, optical amplifiers and active devices for more than 20 years



Very large (and often unexpected) field of expertise.

Pionnering achievements



Numerous results were not released (confidentiality)



ZBLAN glass compositions were characterized in 1980.
[Furukawa (Shibata & Oshawa) paper appeared in 1984]



The first ZBLA:Nd laser was made in 1978 in collaboration with P.Brun's laboratory at Rennes University

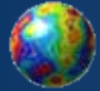


Lasing effect was accidentally observed in 1984 in a Nd-doped fiber supplied to the French CEA

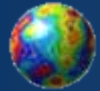


Low loss optical fibers (< 1 dB/km) have been obtained.
Development steps have been identified

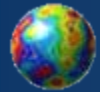
This talk intends



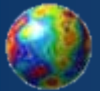
To outline some achievements (Not an exhaustive review!)



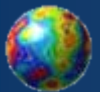
To discuss problems in relation to fiber lasers, amplifiers and sources.



To complete ambiguous or misleading informations

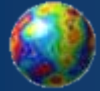


To draw prospects for future realizations



To make the ground for possible interactions

Interactions, collaborations



JPL (NASA), large NA fibers (1985)



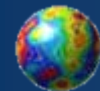
France Telecom (CNET), ORC



Various German companies and universities



Large astronomic observatories (VLT, Hawaii)



Researchers and groups from this audience



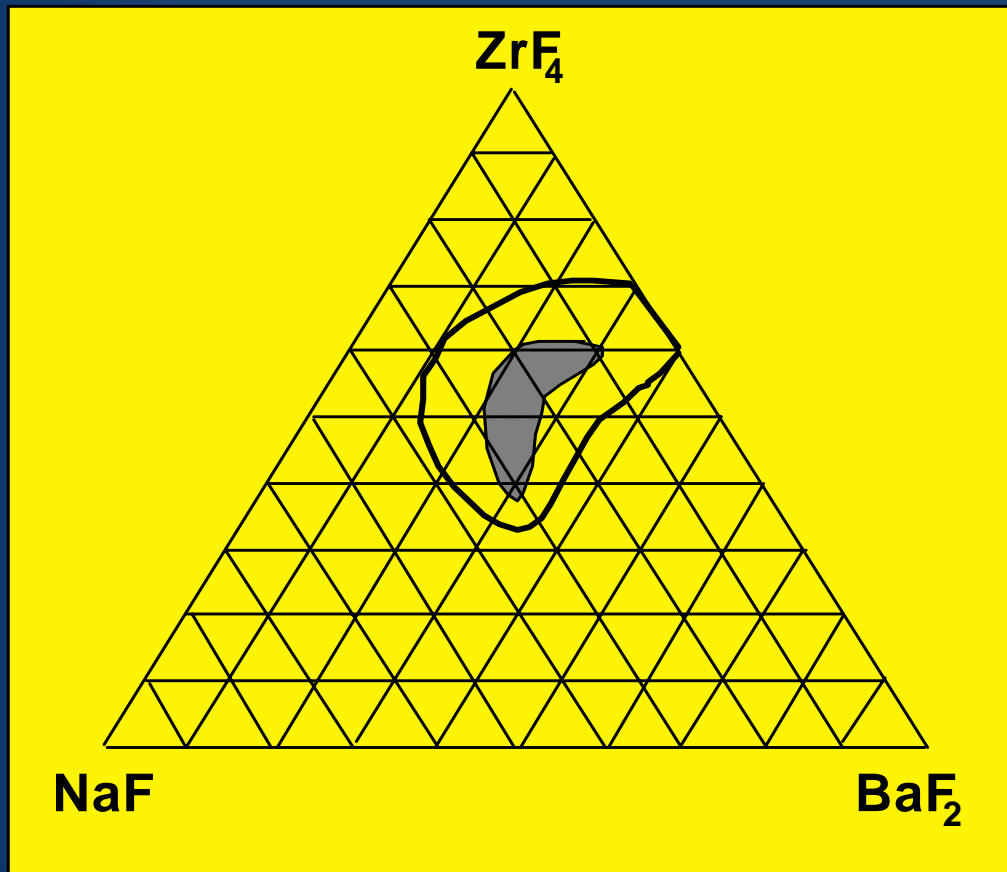
Close collaboration with COPL, Laval Univ, Québec



FLUORIDE GLASS TECHNOLOGY

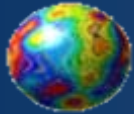


21 Glass composition



Initial system
(1975)

Fluoride glass families



Most studies focused on fluorozirconates based on ZrF_4 and HfF_4



Other fluoride glasses are formed with AlF_3 , GaF_3 and InF_3 as main glass formers



Significant differences are observed in:

- Chemical durability**
- Glass stability**
- Mechanical strength & hardness**
- Phonon energy**

Typical glass compositions

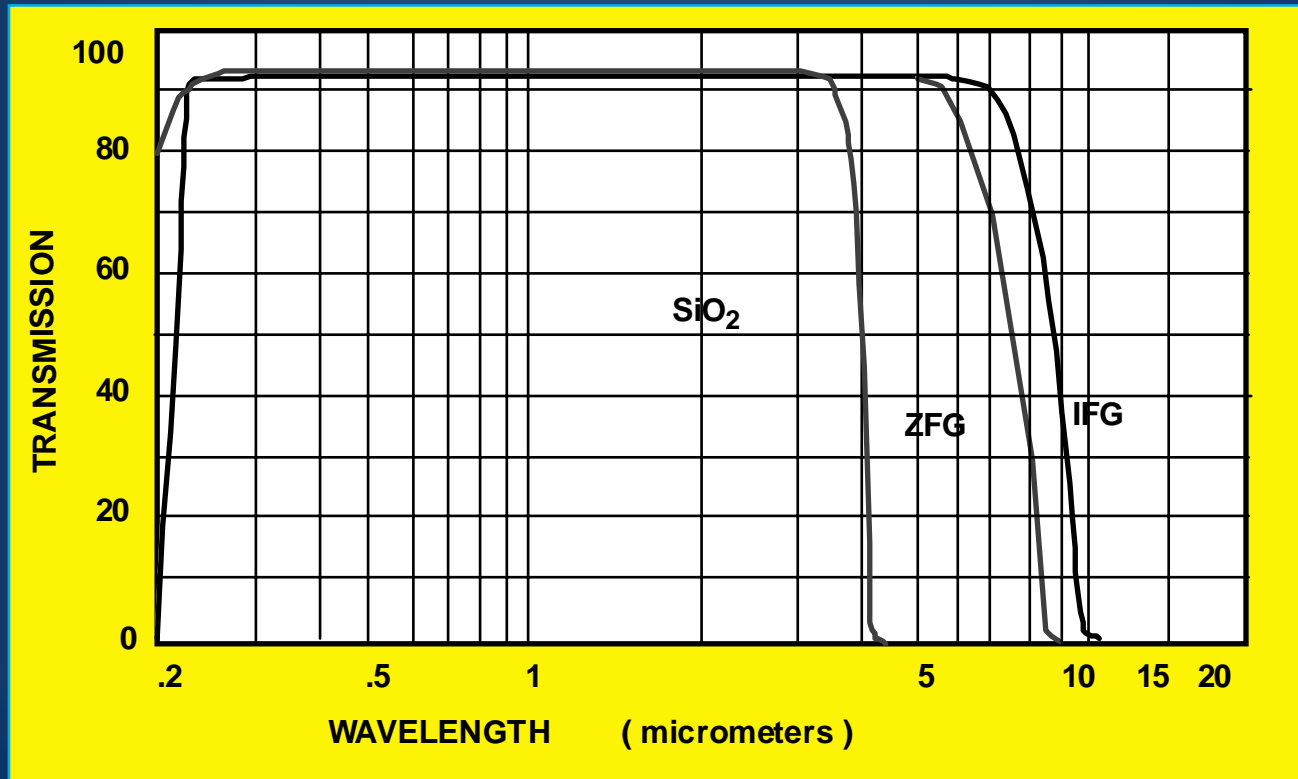
Glass	COMPOSITION (mol %)	n_D
ZBLA	57 ZrF ₄ , 34 BaF ₂ , 5 LaF ₃ , 4 AlF ₃	1.519
HBLA	57 HfF ₄ , 34 BaF ₂ , 5 LaF ₃ , 4 AlF ₃	1.504
ZBLAN	53 ZrF ₄ , 20 BaF ₂ , 5 LaF ₃ , 4 AlF ₃ , 20 NaF	1.498
ZBSFCl	60 ZrF ₄ , 20 BaFCl, 20 SrFCl	1.542
YABC	20 YF ₃ , 40 AlF ₃ , 20 BaF ₂ , 20 CaF ₂	1.440
IZBS	40 InF ₃ , 20 ZnF ₂ , 20 SrF ₂ , 15 BaF ₂ , 5 CaF ₂	1.495
PGICZ	30 PbF ₂ , 22GaF ₃ , 13 InF ₃ , 18 CdF ₂ , 13 ZnF ₂ , 2 GdF ₃ , 2 NaF ($n = 1.595$)	

General physical properties

PROPERTY	HMFG	ZBLAN
Glass transition temperature (°C)	200-450	260
Coefficient of Thermal Expansion (10^{-7} K^{-1})	140-210	180
Density (g/cm ³)	4-6	4.14
Young Modulus (GPa)	50-60	54
Vickers hardness (kg/mm ²)	200-270	210
Poisson ratio	0.25 – 0.35	0.30
Refractive index n_D	1.45 – 1.60	1.500
Non linear refractive index n_2 (10^{-13} esu)	0.8 – 0.9	0.85
Abbe Index ν	60 – 80	75
dn/dT	$1 \cdot 10^{-5}$ - $2 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$
Cp (J / g at.K)		24.9

Optical transmission

Optical transmission of samples 4 mm thick



STRUCTURE: the vacancy model



Numerous structural investigations show the high coordination number of the vitrifying cations: 8 (Zr) or 6 (Al, Ga, In).

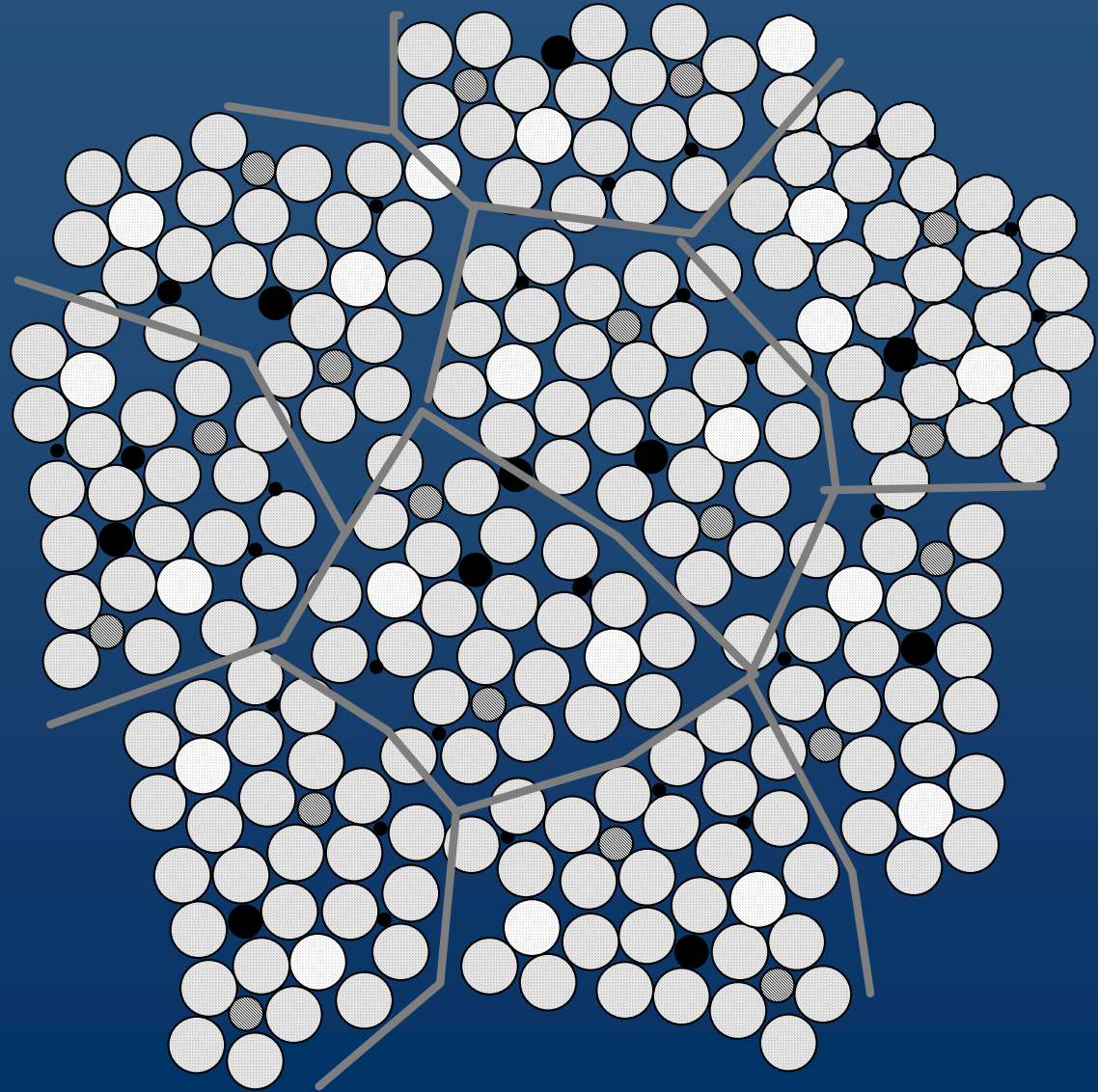


The vitrifying network is constructed from the association of the MF_6 or MF_8 polyhedra with large cations Na^+ , Ba^{++} as modifiers.



The vacancy model offers an alternative description:
A disordered packing of large ions (F^- and Ba^{++}) in which small cations are inserted. This packing contains vacancies that are mobile in the liquid state.

Bidimensional picture





GLASS PROCESSING



22 GLASS SYNTHESIS



Fluoride glass synthesis includes melting, fining, casting and annealing steps



Specific features are low melt viscosity, volatilization, devitrification and hydrolysis.



Water action is critical. To overcome the problem various solutions have been reported:

- Reactive atmosphere processing
- Ammonium bifluoride processing
- Dry processing



Optical quality samples



Samples prepared at room atmosphere from current starting materials exhibit numerous defects:

- Cords and syrups
- « Stones » and inclusions
- Bubbles
- Crystals
- Composition fluctuations



Manufacturing of optical quality samples ($\Delta n < 10^{-6}$) is difficult and time consuming.



Several parameters must be considered and optimized

23 Fiber manufacturing

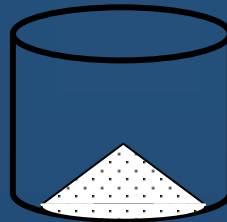
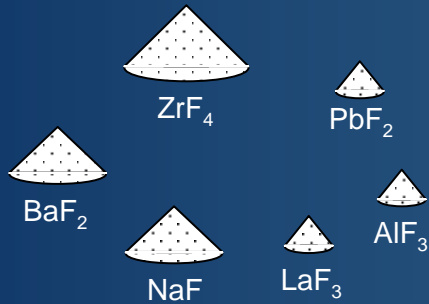
Powders

Melting

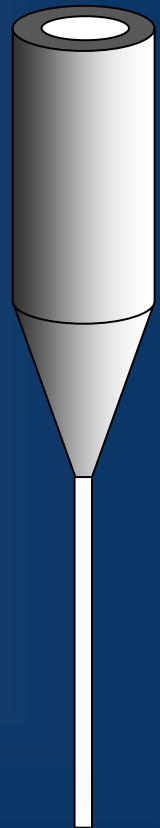
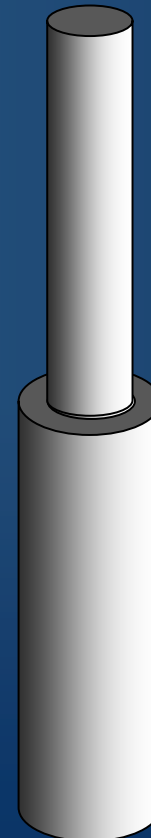
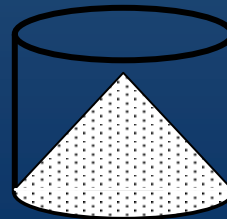
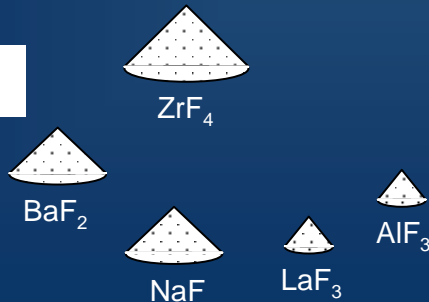
Preform

Fiber

Core

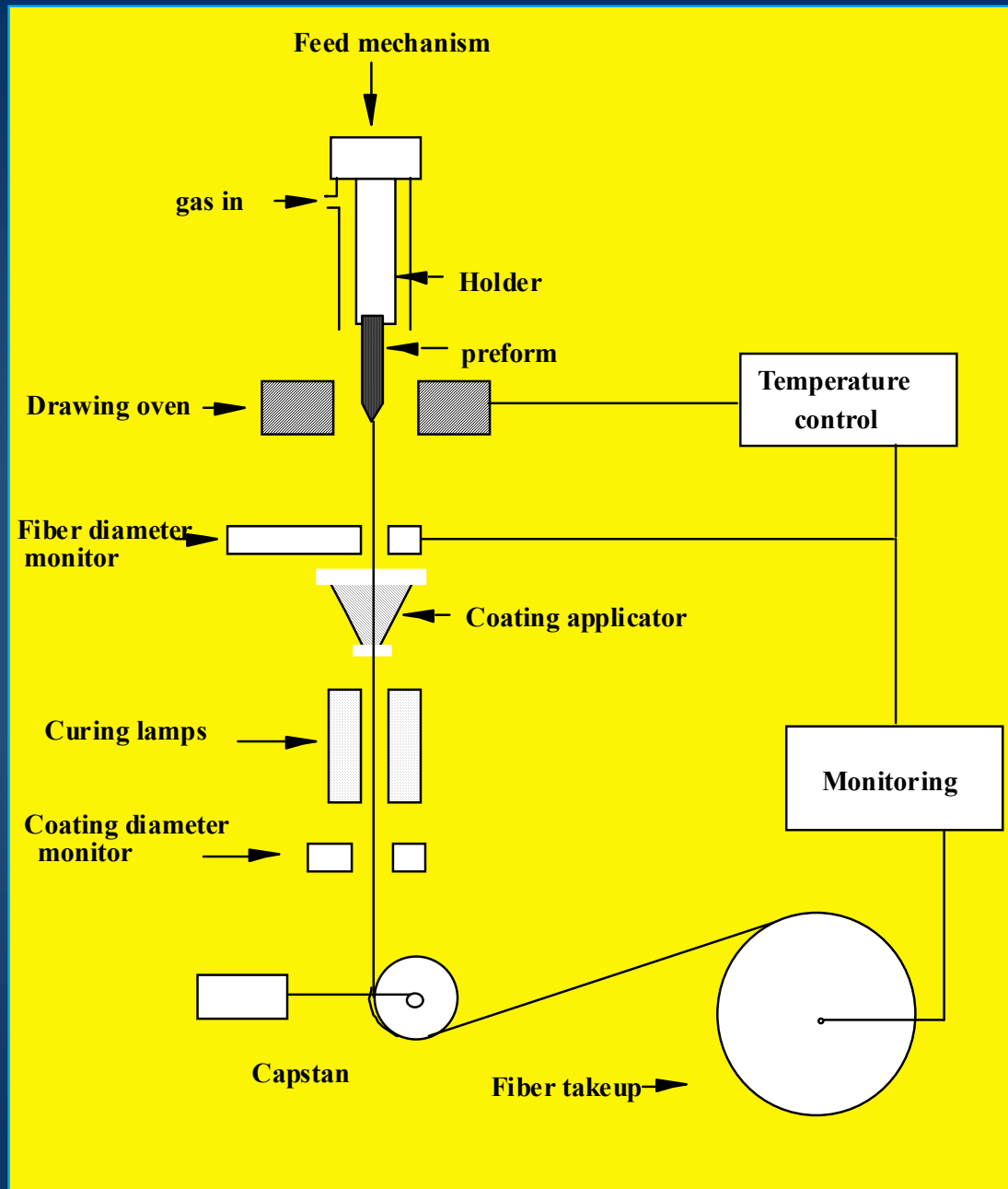


Cladding



Fiber drawing

Fluoride glass fibers are drawn using glass preforms which are processed from high purity glasses processed in a very dry and clean atmosphere. The optical and physical characteristics of the preform determine to a large extent the structure and the optical properties of the fiber.



Critical aspects of HMFG fibers



Fiber drawing adds defects to the preexisting defects in the preform



Various parameters must be optimized:
Time, temperature, preform size, atmosphere
(water, contaminants, dust)



Main contribution to optical losses arise from core defects



Quality of core/cladding interface is critical



SPECIFICATIONS



General features:

optical fiber must be



Strong enough to survive in any case



Transparent in operating window (low optical losses)



Durable in ambient air and humidity



Stable optically and mechanically *vs* time and temperature



Comply with optical specifications

Rare earth doped fibers must be



Homogeneous (no clustering)



Host the convenient amount of active ions.



Have minimum background losses

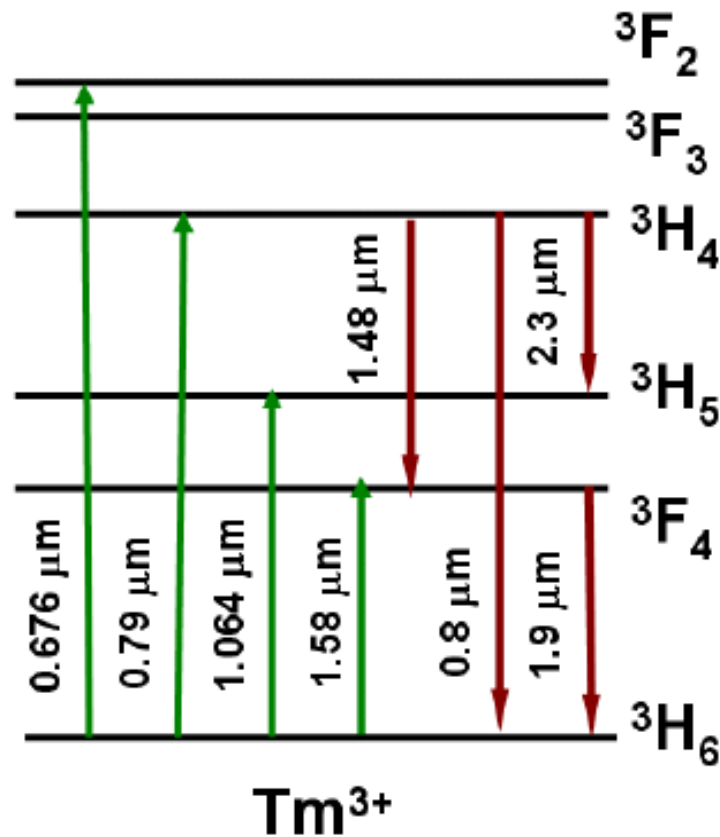


Allow co-doping (e.g. Yb/Er)

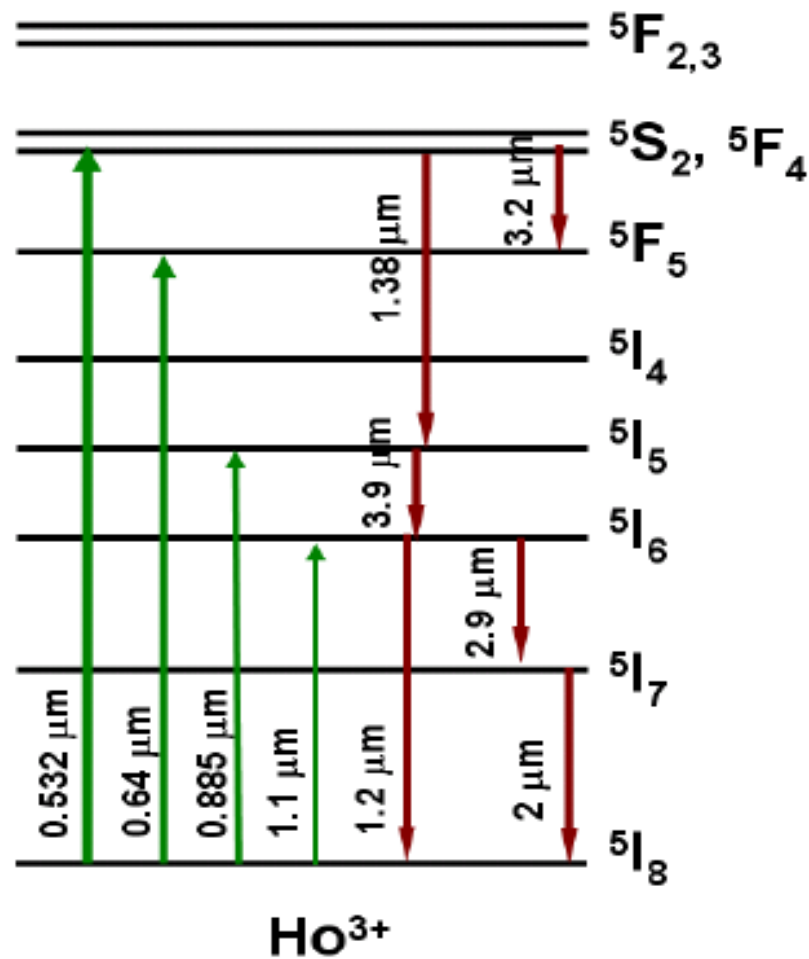


Withstand high energy pumping

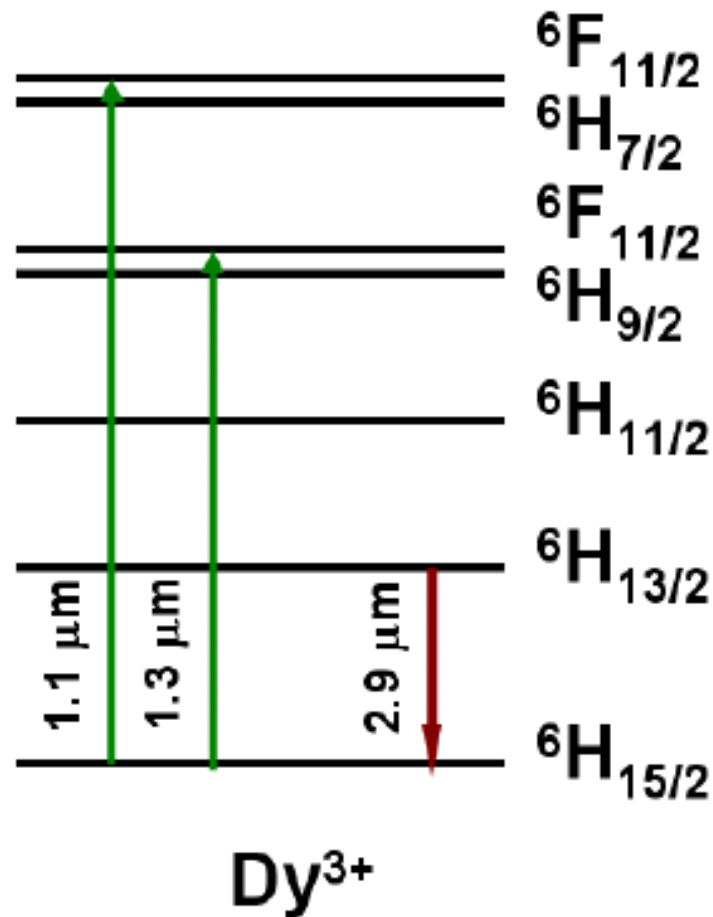
Rare earths for mid IR emission



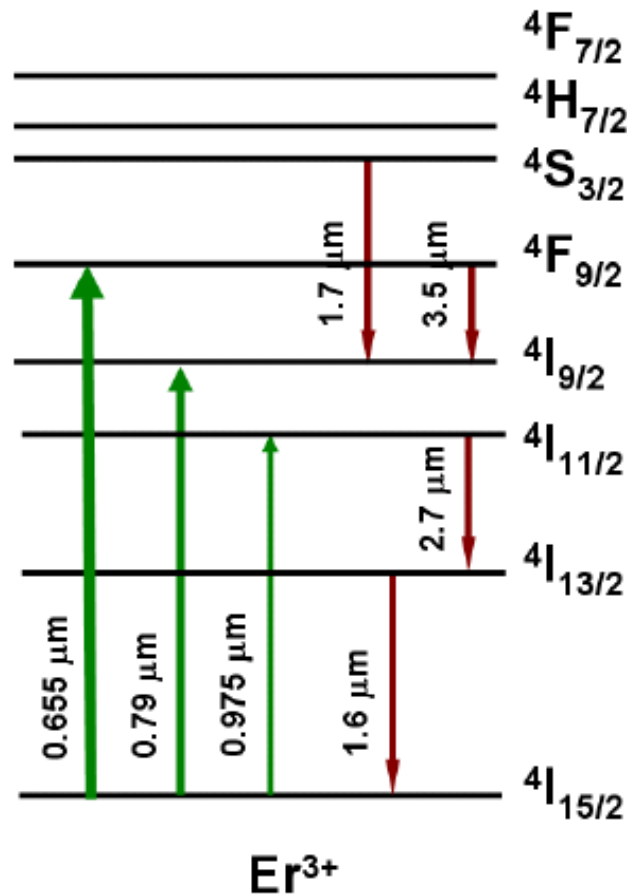
Rare earths for mid IR emission



Rare earths for mid IR emission



Rare earths for mid IR emission



High power and supercontinuum



Fiber must withstand large pump power



Limitations arise from extrinsic defects
(Intrinsic damage threshold is largely unknown)



Power in cladding must be controlled



High non linear parameters are desirable



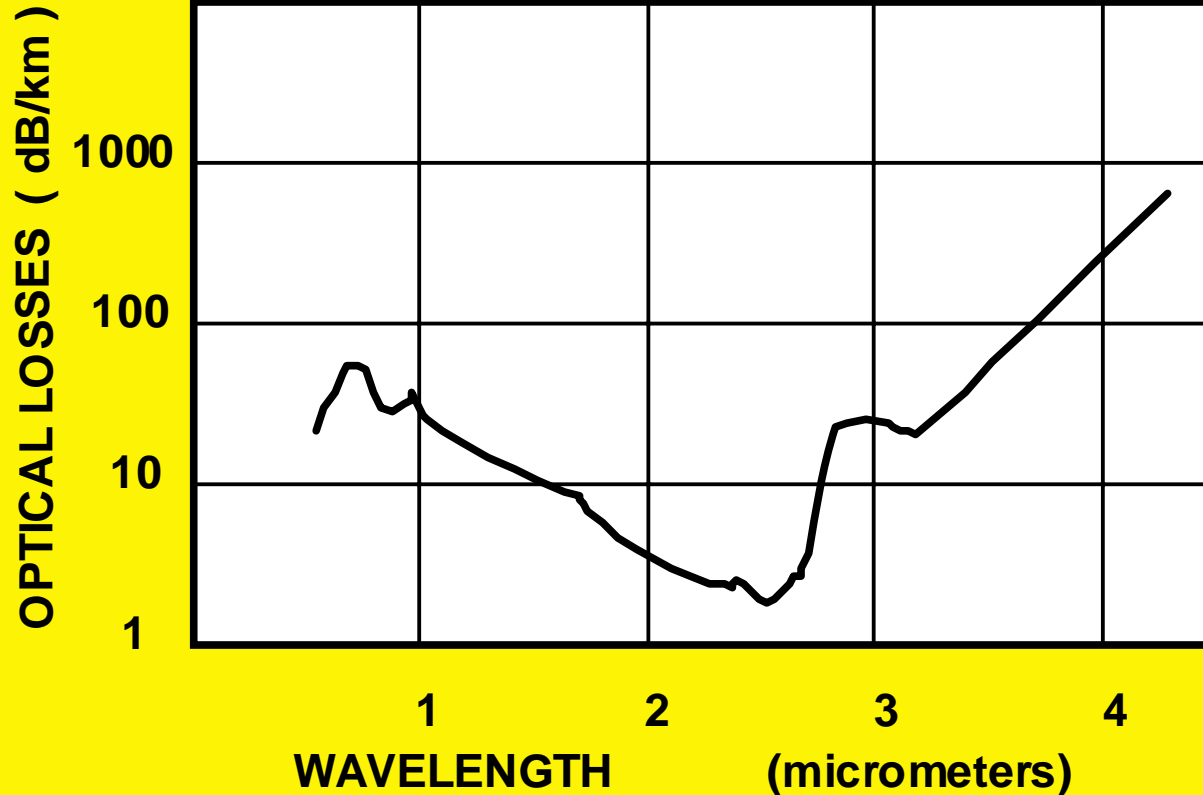
Reliability of resonator, splicing and end faces



ACHIEVEMENTS

Optical transmission: fibers

Typical losses of a multimode fiber



Optical transmission: fibers

Typical losses of a singlemode fiber

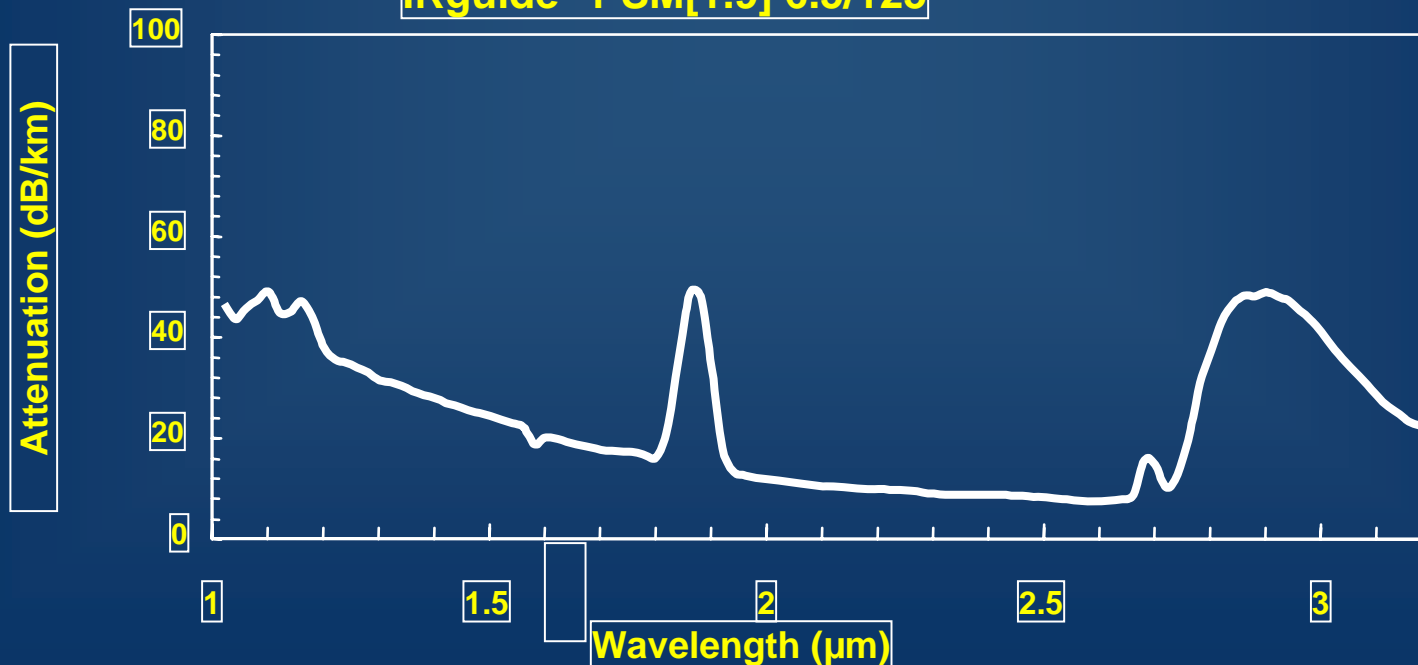
Ø core / Ø cladding : 6.5 / 125 µm

Attenuation at 2.5 µm : 5 dB / km

Cut-off wavelength : 1.9 µm

Attenuation at 3.2 µm : 20 dB / km

IRguide -1 SM[1.9] 6.5/125



Type of fibers



Multimode

Single mode

Polarization maintaining

Low birerengence

Rare eath-doped

Double-clad

D-shasped,

Ring-core (M-shaped)

High NA

ZBLAN fiber lasers



Intense activity in the 80's (CNET, BT...)



Development in various german labs and companies (90's):
FSU Iena, Techn. Univ. Berlin, Laser Zentrum Hannover,
Laser Zentrum Hambourg, Lasos, Guided Color Techn.,
Unique Mode, Linos, Philips...

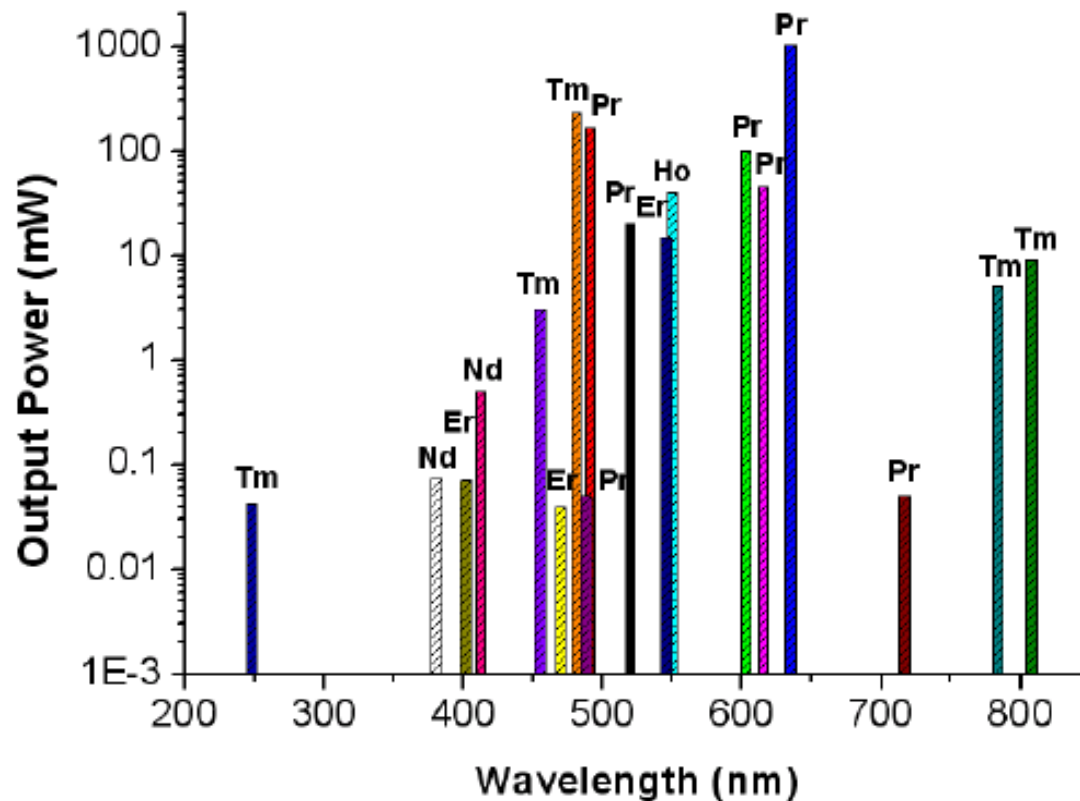


ZBLAN fibers have hugely increased the number of laser lines

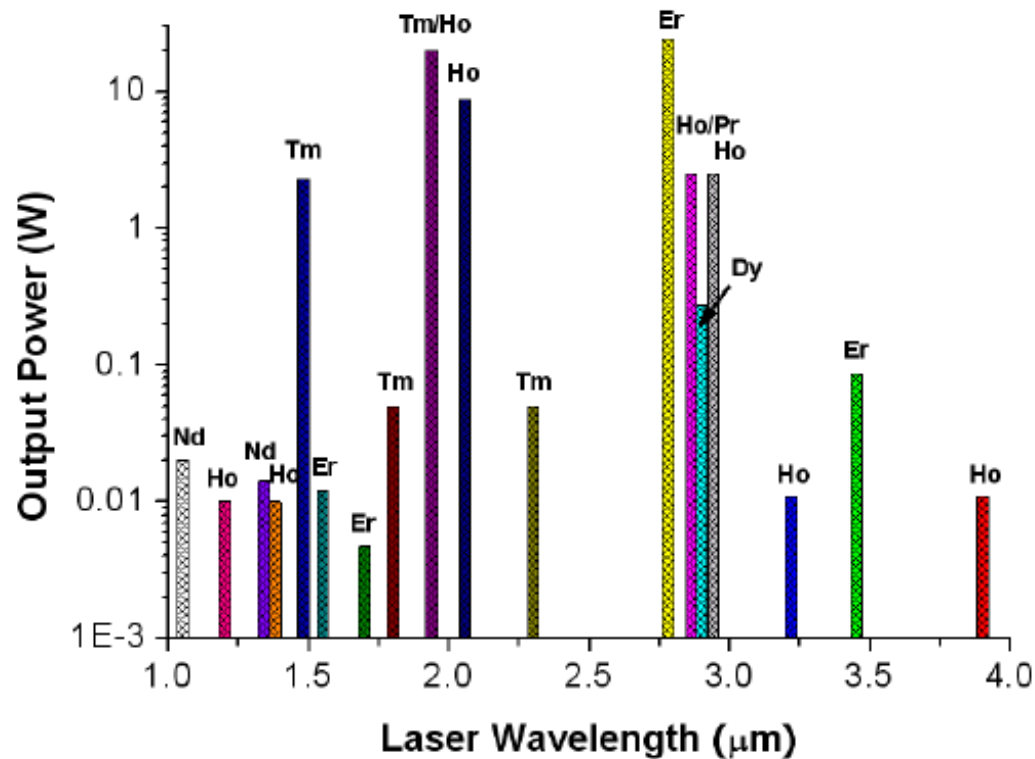


Marketing issues are heavier than technical problems

ZBLAN fiber lasers: Up conversion



ZBLAN fiber lasers: Mid IR



Supercontinuum



Significant achievements with ZBLAN fibers



Various parameters: fiber length, attenuation, pump power, pump frequency, pump wavelength, N.A., dispersion, fiber geometry...



Laboratory results



Available systems

Supercontinuum using short fibers

From Toyota Technological Institute (Prof. Y. Ohishi)

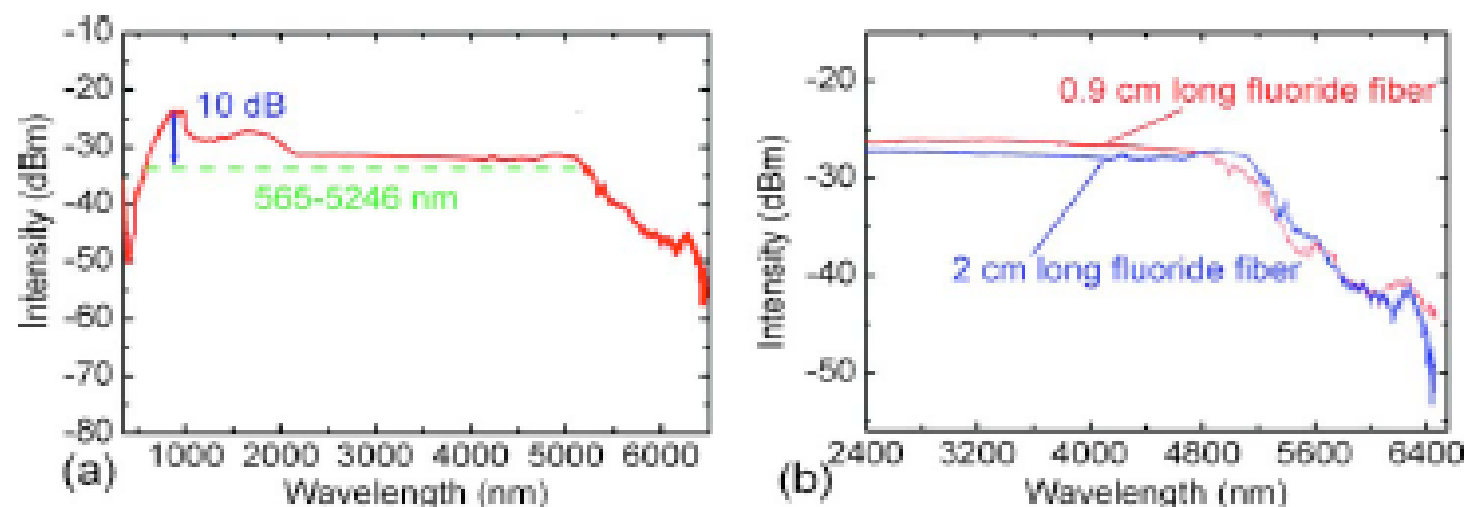


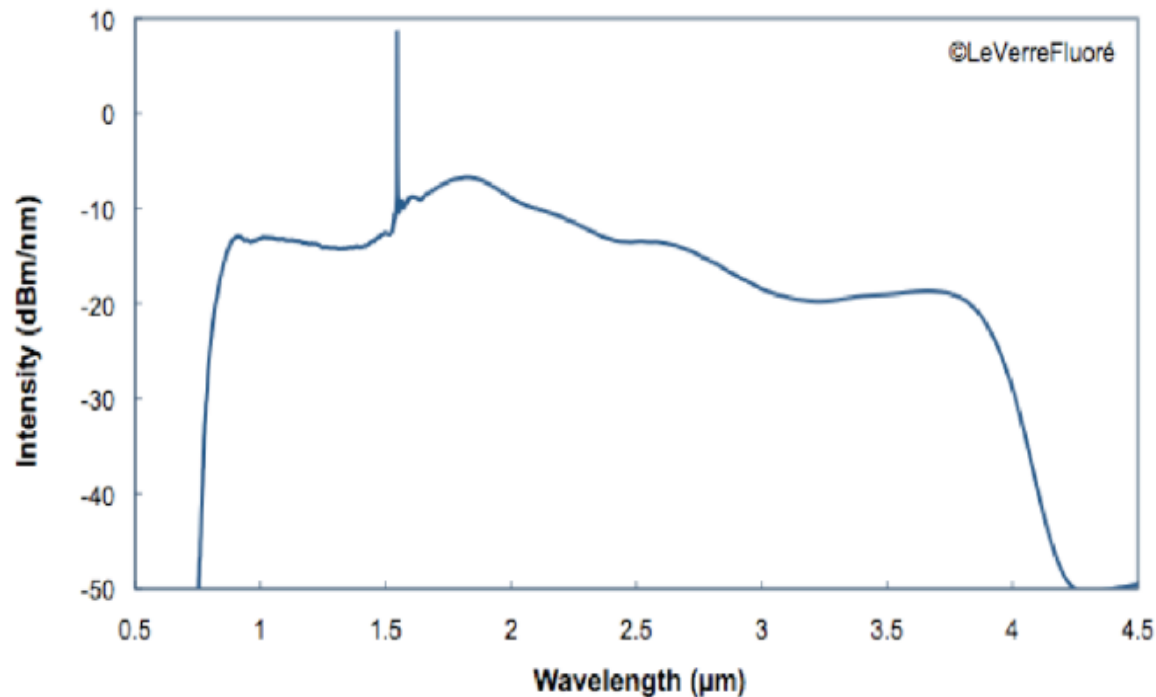
FIG. 2. (Color online) (a) The measured SC spectra from the 2-cm-long fluoride fiber when the average pump power of 1450 nm femtosecond laser was fixed at 20 mW (the corresponding peak power is about 50 MW). (b) A comparison of the long-wavelength edge of SC spectra in 0.9 or 2 cm long fluoride fiber.

Supercontinuum

Current ZBLAN source



Typical IRguide® SC-01 Spectrum





PROBLEMS AND PROSPECTS



Practical questions



Mechanical strength.



Aging



Chemical durability



Thermal stability



Optical specifications

Fiber strength



Failure occurs on defects, most of them extrinsic



Intrinsic strength limited by chemical bonding



Tensile strength improve by CTE adjustments



Static fatigue may be controlled by relaxation

Chemical durability



Water, water, water



Liquid water must not be in contact with glass surface



Fiber is protected by coatings, jacketing, cabling.



End faces make problem. Solutions exist !



Fluoride fibers in use in industrial environment
for more than 10 years.

Bragg gratings in fluoride



Pioneering achievements in CNET (FT)



But time consuming and Cerium doping



Reliable Bragg gratings obtained by femtosecond lasers
at COPL, Laval University, Québec

Damage threshold



Is critical for high power lasers and supercontinuum



Low values have been observed in real fibers,
in relation to extrinsic defects



High values measured (ISL)



Femtosecond experiments implemented at Laval University,
Suggest that intrinsic damage threshold could be higher
in ZBLAN than in silica!

Control of fiber defects



Identification: crystals, bubbles, metal particle, carbon...



Processing parameters to be adjusted



Contamination of interfaces



Glass stability in high NA fibers



Adjustment of thermal expansion coefficients

Extending optical window



Requires using Indium-based glasses free of Zr and Al



Less stable compositions make more difficult to reach low background losses



Encouraging laboratory results



Development in progress

Photonic crystal fibers



Large potential



May be achieved with ZBLAN glass



Probably more difficult than silica or chalcogenides



Thermal properties of ZBLAN offer extended possibilities

CONCLUSIONS



The potential of fluoride fiber lasers is very large



... But FG fiber lasers are just emerging



Most technological problems are identified



Both laser and supercontinuum sources are available



Photonic crystal fibers to be developed

ACKNOWLEDGMENTS



The scientific community for its continuous interest



All of you for your attention

Application of lacunar model to ZBLAN glass

Molar volume of ZBLAN glass is 8.10 cm^3 and $\Delta C_p = 14.2 \text{ J.mol}^{-1}.\text{K}^{-1}$ while I have measured $\Delta\alpha = 1.2 \cdot 10^{-4} \text{ K}^{-1}$ (dilatometry), which leads to $e_v = 132 \text{ KJ. mole}^{-1}$.
The rate of vacancy formation is $8 \cdot 10^{18} \text{ K}^{-1} \text{ cm}^{-3}$.

With 120 K as the estimated difference between T_g and T_K the gross number of vacancies is $N \approx 10^{21} \text{ cm}^{-3}$ at T_g